

PEER-REVIEWED PAPER

The Physical Behavior of Arabinoxylans in Model Brewing Solutions

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ABSTRACT

This paper reports on the filtration and rheological properties of arabinoxylan polymers of average molecular weights (MW) of 66,000, 278,000, and 294,000. Model beers were made with 0.5 g of maltose mixed with 5 mL of 100% ethanol made up to 100 mL by the addition of a sodium acetate buffer (pH 4.0) solution. Arabinoxylan polymers were added to this model beer at levels of 25, 50, 100, 250, 500, 1,000, 2,000, 3,000, 4,000, and 5,000 mg/L. At most gum concentrations and temperatures, the solutions behaved in a Newtonian fashion. Critical concentrations in which polymer entanglement occurred (c^*) were determined to be 1,050 and 738 mg/L for the 278,000- and 294,000-MW polymers, respectively. The change in viscosity with temperature could be described by the Arrhenius model, and activation energies ranged from 5.93 to 18.0 kJ/mol. The filtration of the model beers containing arabinoxylans through cellulose acetate filters could be described by the Standard blocking law. This law could be used to calculate the maximum filtrate volume (V_{max}) and the initial rate of filtration (Q_{init}). Arabinoxylan concentration had a significant effect ($P < 0.05$), reducing V_{max} and Q_{init} values as the concentration increased. Membrane pore diameter size also had a significant effect ($P < 0.05$), increasing V_{max} and Q_{init} as the pore diameter size increased. It was interesting to notice that while arabinoxylan MW had a significant ($P < 0.05$) effect on V_{max} and Q_{init} , medium-viscosity-arabinoxylan model beers had the highest V_{max} values, while low-viscosity-arabinoxylan model beers had the lowest V_{max} values at all polymer concentration levels, except 25 mg/L. Scanning electron microscopy of the results indicated that low-viscosity arabinoxylans could penetrate the membrane surface more easily than could medium- and high-viscosity macromolecules because of the shorter polymer chains, thus enhancing the membrane clogging.

Keywords: arabinoxylan, intrinsic viscosity, membrane filtration, Q_{init} , viscosity, V_{max}

SÍNTESIS

Esta presentación informa sobre las propiedades reológicas y filtrabilidad de polímeros de arabinoxilanos con peso molecular promedio de 66.000, 278.000 y 294.000. Se prepararon modelos de cerveza con 0,5 g de maltosa mezclada con 5 mL de etanol (100%) llevado a 100 mL con una solución amortiguadora (buffer) de acetato de sodio (pH 4,0). Se añadieron polímeros de arabinoxilanos a este preparado para alcanzar niveles de 25, 50, 100, 250, 500, 1.000, 2.000, 3.000, 4.000, y 5.000 mg/L. Estas soluciones se comportaron, en la mayoría de las concentraciones y temperaturas probadas, de forma Newtoniana. La concentración crítica (c^*) en que ocurrió el enmarañado de los polímeros fue 1.050 y 738 mg/L para los polímeros de 278.000 y 294.000 peso molecular, respectivamente. El cambio de la viscosidad con la temperatura se pudo describir por el modelo Arrhenius, y las energías de activación variaban de 5,93 a 18,0 kJ/mol. La filtración de las soluciones modelo con arabinoxilanos a través de filtros de acetato de celulosa pudo ser descrito por la ley de bloqueo estándar. Esta ley permitió calcular el volumen máximo de filtrado, V_{max} , y la tasa inicial de filtración, Q_{mic} . La concentración de arabinoxilano tiene un efecto significativo ($P < 0,05$), observándose una reducción en los valores de V_{max} y Q_{mic} al aumentar la concentración. El diámetro de los poros de la membrana también tuvo un efecto significativo ($P < 0,05$), aumentando V_{max} y Q_{mic} al aumentar el diámetro de los poros. Fue interesante notar que si bien el peso molecular de la arabinoxilano tuvo un efecto significativo ($P < 0,05$) sobre el V_{max} y Q_{mic} , fueron las soluciones modelos con arabinoxilanos de viscosidad mediano las que tuvieron los más altos valores de V_{max} y (contrario a lo esperado) las soluciones modelos con arabinoxilanos de viscosidad baja dieron los más bajos valores de V_{max} a todas las concentraciones de polímeros a excepción de 25 mg/L. La microscopía por escaneo de electrones de la superficie de la membrana indicaba que los polímeros de baja viscosidad pudieron penetrar la membrana con más facilidad que las macromoléculas de viscosidad media y alta debido a sus cadenas más cortas, así tapando los poros de la membrana más efectivamente.

Palabras claves: arabinoxilano, viscosidad intrínseca, filtración por membranas, Q_{mic} , viscosidad, V_{max}

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Introduction

During the last quarter century, brewing unit operations have evolved in order to increase the speed and efficiency of the brewing process, improving the quality of beer available to the consumers. Some of these advances include production of high-gravity beers, reduction of cellar storage times, increase of transfer rates, and the use of new filter technologies. However, during these last 25 years, substantial processing problems have also been related to nonstarch polysaccharides in wort and beer (16). Although both arabinoxylans and β -glucans have been implicated, arabinoxylans have received little attention from brewing researchers.

Arabinoxylans contribute to beer foam stability (1). However, these substances also produce viscous aqueous solutions (18), which can lead to serious production problems, including reduced rates of wort separation, low recovery of malt extract,

shortened filter life, diminished rates of beer filtration, and the formation of gels, hazes, and sediments in beer (2,6,22). The polymer consists of β -(1,4)-D-xylopyranosyl-linked units with single L-arabinofuranosyl branches connected to the backbone either by the α -(1,2) or α -(1,3) links (25) as shown in Figure 1. The reader is referred to the accompanying review (3) for full details as to the structure, properties, and occurrence of this polymer. Nonetheless, it is important to review reports of the polymer's effects on wort and beer physical properties.

At the low concentrations encountered during brewing (<2% [w/v]), arabinoxylan solutions behave as Newtonian liquids, meaning their apparent viscosities are not dependent on the shear rate at which they are measured (8). However, it is not clear if long-term shear can increase Newtonian viscosities (η), as in the case of β -glucan solutions (12). The viscosities of these solutions are, nonetheless, dependent on arabinoxylan concentration and temperature.

With regard to concentration, there are two concepts useful to understand. The first of these is the critical concentration (c^*), which corresponds to the onset of coil overlap between the polymer chains. At lower polymer concentrations, the viscosity increases in a linear fashion with increasing concentration. Above a certain critical arabinoxylan concentration (c^*), the slopes change abruptly to higher values (slope \cong 2). The critical concentration marks the onset of significant polymer overlap and interpenetration and the transition from dilute solution conditions (in which individual polymer molecules are present as isolated chains) to semidilute solutions (in which the total hydrodynamic volume of the individual chains exceeds solution volume) (19).

The second useful term employed by polymer rheologists is that of 'intrinsic viscosity' ($[\eta]$). When a polymer is introduced into the fluid, it disturbs the flow streamlines, causing an additional energy dissipation, and as a result, the viscosity of a solution is greater than that of the pure solvent (η_s). The intrinsic viscosity can then be defined as the limiting value (lim) of either reduced (η_{red} , the ratio of specific viscosity to concentration) or inherent (η_{inh} , the ratio of the natural logarithm of relative viscosity to concentration) viscosity as the concentration (c) approaches zero:

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{red}) = \lim_{c \rightarrow 0} (\eta_{sp}/c) \quad (1)$$

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{inh}) = \lim_{c \rightarrow 0} (\ln \eta_{rel}/c) \quad (2)$$

in which relative viscosity (η_{rel}) is the ratio of the solution to solvent viscosity, and the specific viscosity (η_{sp}) is the difference between the solution and solvent viscosity divided by the solvent viscosity (5). The intrinsic viscosity or the limiting viscosity number is a characteristic property of an isolated polymer molecule in a given solvent and is a measure of the hydrodynamic volume occupied by the polymer, which primarily depends on the molecular weight (MW), chain rigidity, and solvent quality (15,19).

Various empirical models, such as those of Huggins and Kramer (12), have been developed to express solution viscosity as a function of concentration to determine the intrinsic viscosity. Many of these expressions have only limited application (26). As the polymer concentration increases (up to a critical concentration, c^*), the macromolecular chains begin to overlap.

The viscosity-concentration relationship in moderately concentrated solutions can be described by the Martin equation (26). In the semidilute regime, the product of concentration (c)

by intrinsic viscosity ($[\eta]$) ranges from 1.0 to 10.0. Above the critical concentration, the viscosity of the solution increases sharply and $c[\eta] > 10$. Furthermore, Kasaai et al. (13) reported the critical concentration to be $1/[\eta]$.

Kozicki and Kuang (14) proposed a method that yields an independent evaluation of the intrinsic viscosity and does not involve extrapolation:

$$\eta_{sp} = [\eta]c + b * c^d \quad (3)$$

in which the intrinsic viscosity ($[\eta]$) and the b and d constants can be determined by the least squares fitting of the equation to the data.

Since viscosity as a function of polymer concentration is linear at a low concentration and then rises exponentially with increasing concentration, in one of the few brewing reports, Linemann and Kruger (17) determined the c^* of β -glucan solutions. They found a correlation of the relationship of the reciprocal of the logarithm of the relative viscosity $1/\log(\eta_{rel})$ to gum concentration (in which relative viscosity is η/η_s). These authors argued that a break in the linear curve occurred at c^* .

As one might expect, the intrinsic viscosity of a polymer depends on its MW. The intrinsic viscosity of polymers has been customarily been expressed by the Mark-Houwink-Kuhn-Sakurada (MHKS) equation

$$[\eta] = K * M^a \quad (4)$$

in which M is the MW, and K and a are constants for a given solute-solvent system, the latter being characteristic of the molecular conformation (26). This relation can be applied to determine the exponent a by use of a simple logarithmic transformation. Thus, the conformation of arabinoxylan polymers in the solution can be investigated by the measurement of $[\eta]$ at different MWs. The values of the exponent a are reported to be 0 for rigid spheres, 1.7–2 for rigid rods (26), and 0.5–0.8 for flexible polymers (5). It was also observed experimentally that stiff polymers have values ranging from 0.8 to 1.2 (26).

During brewing, filtration can be accomplished either by depth retention or by straining, such as in membrane filtration. High arabinoxylan and β -glucan levels have the most catastrophic effect on the straining filtration when beer is passed through submicron filters.

Because of the substantial filtration problems that can occur, brewers have devised membrane filterability tests based on the measurements of a beer flow at set upstream pressures through

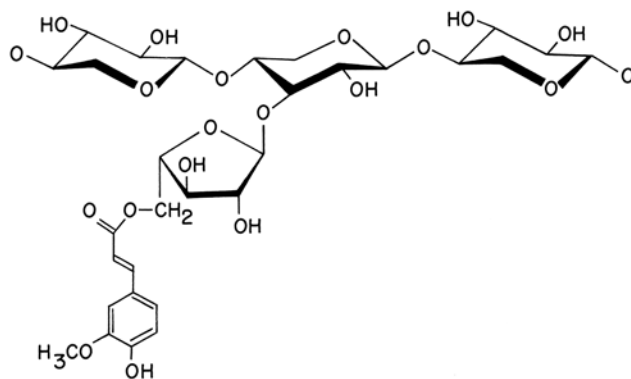


Figure 1. Structure of a portion of a β -(1,4)-xylan chain substituted at the O-3 atom of the residue with a 5-O-trans-feruloyl-L-arabinofuranosyl substituent. (Reprinted, with permission, from Fincher and Stone [4]; ©American Association of Cereal Chemists)

a membrane filter. The results of these tests are generally characterized in terms of the maximum volume of liquid that can be filtered through a membrane filter (V_{\max}) and the initial flow rate (Q_{init}) (24):

$$t/V = t/V_{\max} + 1/Q_{\text{init}} \quad (5)$$

in which t is the time and V the filtrate volume. This relationship is referred to as the Standard blocking law described by Hermans and Bredee (7), who considered that a filter consists of a set of parallel capillary tubes of constant length whose diameter decreases gradually over time by adsorption of precipitates (i.e., arabinoxylan polymers). Stewart et al. (23) conducted a study on cold sterile filtration using beer brewed from 24 commercially available malt samples. The results from this filtration test showed that beer arabinoxylan content was negatively correlated with the maximum volume of beer that can be filtered through a membrane ($P < 0.01$).

Materials and Methods

The schematic diagram in Figure 2 outlines the experimental plan of this study. Low-molecular-weight (LMW), medium molecular-weight (MMW), and high-molecular-weight (HMW) wheat arabinoxylans of average MWs of 66,000, 278,000, and 294,000, respectively, were obtained from Megazyme International Ltd. (Wicklow, Ireland) and were used in preparation of model beers. Within each MW group, 10 different model beers containing 5% (v/v) of ethanol and 0.5% (w/v) of maltose sugar were prepared by dissolving 5,000 mg of arabinoxylan

per L and making dilutions to get the final arabinoxylan concentration (i.e., 25, 50, 100, 250, 500, 1,000, 2,000, 3,000, 4,000, and 5,000 mg/L).

A stock 5,000-mg/L suspension was prepared with arabinoxylan powder (0.5% [w/v]) in a 200-mL beaker, followed by the addition of 2 mL of 100% ethanol to dampen the powder and prevent clumping upon the addition of buffer. The contents were then lightly mixed for 20 to 30 s. Immediately after that, 85 mL of deionized (DI) water was added to the beaker, followed by continuous vigorous stirring. After 8 min, when the boiling started, the beaker was covered with aluminum foil to prevent the formation of a “skin” on the top of the solution. While stirring continuously with a stir bar for another 10 min, the arabinoxylan was completely dissolved, after which the heater was turned off. The solution was cooled down to room temperature with continuous stirring for another 20–30 min.

The final composition of model beers was adjusted by adding 5 mL of 2 M sodium acetate buffer (pH 4), followed by the addition of 0.5 g of maltose sugar (to give 0.5% [w/v]) and 5 mL of 100% ethanol (to give 5% [v/v]). The pH was finally adjusted dropwise with 1 M NaOH or 1 M HCl, after which the volume was adjusted to 100 mL with DI water. These dropwise additions had negligible effects on the ionic strength of the solution.

To reach the 10 arabinoxylan concentrations of model beers within each MW group, the 5,000-mg/L suspension was diluted by adding a defined amount of solution buffer (pH 4), which contained 0.5% (w/v) of maltose sugar and 5% (v/v) of ethanol. Finally, all model beers were refrigerated at 4°C over-

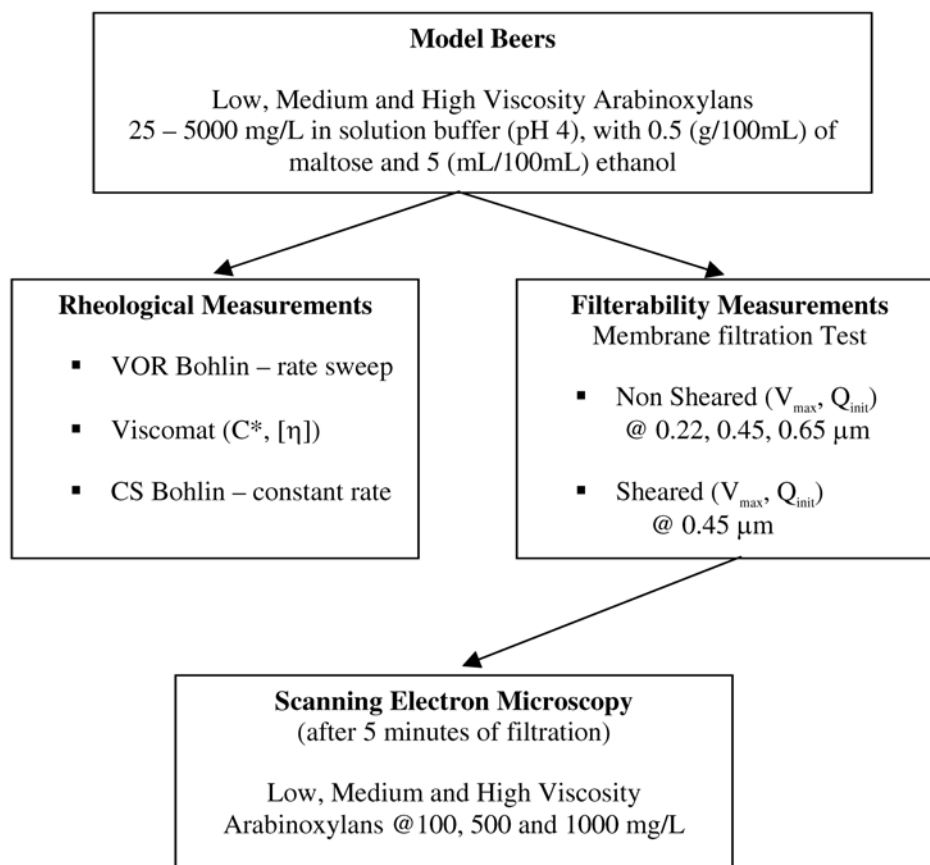


Figure 2. Experimental work plan.

night prior to testing. The final composition of all 30 model beers is shown in Table 1.

The viscosity of the model beers prepared as shown in Table 1 were first examined with a Bohlin VOR controlled rate rheometer (Bohlin Instruments Inc., Cranbury, NJ). A shear rate sweep-up at 5 and 20°C (36.7 to 1,460 s⁻¹) and at 50 and 75°C (116 to 1,460 s⁻¹) was performed with a concentric cylinder fixture (Bohlin C-14 fixture) for 11 min, with an equilibrium time of 10 s, a delay time of 20 s, an integration time of 35 s, a rate sweep option set to “up”, and a continuous rate option set to “on”.

Model beer apparent viscosities were also measured at 20°C with a Viscomat automated capillary rheometer (Pfeuffer GmbH, Kitzinger, Germany). Each viscosity was calculated as the mean value of two successive measurements. The relative maximum error limit in the Viscomat software was preset at 0.5%. From this data, the critical concentration (c*) was determined by regressing (1/log[η_{rel}]) against the concentration (c), after the method of Linemann and Kruger (17) as detailed earlier. A piecewise regression technique with Systat™ 5.05 for Windows (SPSS Inc., Evanston, IL) was used to determine the critical concentration (c*) value as the intersection of two linear curves. The following model was used in the technique in which two linear regression lines were “pieced” together.

$$1/\log(\eta_{rel}) = A0 + A1 * c \quad (\text{in which } c < c^*) \quad (6A)$$

$$1/\log(\eta_{rel}) = B0 + B1 * c \quad (\text{in which } c > c^*) \quad (6B)$$

in which A0 and A1 and B0 and B1 are intercept and slopes above and below c*. The Systat™ 5.05 program iteratively selects values for A0, A1, B0, B1, and c*, which minimizes the residual sum of squares. An alternative method for intrinsic viscosity ([η]) determination, proposed by Kozicki and Kuang (14), and the MHKS equation were applied to describe the relationship between MW and intrinsic viscosity (26).

To perform the rheological measurement of model beers at varying temperatures, a Bohlin controlled stress rheometer (model BR CS 10; Bohlin Instruments Inc.), was used. This unit was equipped with a standard temperature control unit so that the test fluid temperature remained constant throughout the experiments. All the samples were measured at four different temperatures (5, 20, 50, and 75°C). For the measurements performed at 5 and 20°C, cone and plate viscometry was used, utilizing a 4° cone with 40-mm diameter (with a Bohlin CP 4/40 fixture). The shear rate was held constant at 350 s⁻¹ for 20

min, with an equilibrium time of 10 s, a delay time of 15 s, an integration time of 25 s, a rate sweep option set to “up”, and a continuous rate option set to “on”. The tests at 50 and 75°C were performed with a coaxial cylinder fixture (Bohlin C-25 fixture) set at 323 s⁻¹ for 16 min, with the other parameters set like those of the cone and plate fixture. The effect of temperature on apparent viscosity was modeled using an Arrhenius model-type relationship.

The membrane filtration method used for filterability evaluation of the model beers containing increasing amounts of arabinoxylan polymers was based upon the work of Sudarmana et al. (24) as modified by Patelakis (21). The filterability apparatus used in this study consisted of a liquid holding chamber, with a capacity of 20 mL, connected to a membrane holder with 25-mm-diameter disposable cellulose acetate membrane filters (Osmonics Inc., Minnetonka, MN), with pore diameter sizes of 0.22, 0.45, and 0.65 μm. Since it has been reported that filtering behavior of these membrane filters vary by manufacturers' lot, only one lot was used in these experiments (T. Dowgiert, *personal communication*, 1999). The filterability tests were undertaken by filling the holding chamber with cold (0–3°C) test fluid, pressurizing the chamber to 34.475 kPa ± 6.895 kPa (5 psi ± 1 psi) with compressed N₂ gas, and prewetting the filter by quickly opening and closing the stopcock valve above the filter. After zeroing the balance, the actual filtration tests were begun by opening the stopcock. Balance readings were recorded every 10 s for the first 2 min, every 30 s for the next 3 min, and finally, every 2 min for the last 8 min. Thus, 23 measurements were taken over a total of 13 min, and the data were used for model fitting and further calculations of V_{max} and Q_{init} values. Prior to filtration testing, all model beers were kept on ice for 2 h within a temperature range of 0 to 3°C.

Aside from examination of the fit of the Standard blocking law (Eq. 5), the fit of other filtration models, described by Hermans and Bredee (7) (i.e., Cake filtration law, Law of complete blocking, Intermediate law, and Standard blocking law), to the data was examined.

To test the effect of high-intensity shearing on filterability, model beers with arabinoxylan concentrations from 1,000 to 5,000 mg/L were used. The samples were sheared in a Lourdes laboratory blender (Lourdes Industries, Inc., Farmingdale, NY) with the speed control set to 50 for a total of 10 min (approximately $\dot{\gamma} \geq 5,000$ s⁻¹). During shearing, the temperature of the samples increased to 45°C ± 2°C. The samples were then cooled under cold running water to room temperature (23°C ± 1°C). The filterability tests were undertaken immedi-

Table 1. Outline of the composition and suspension codes of model beers

Arabinoxylan concentration (mg/L)	Suspension codes ^a			pH	Ethanol (% [v/v])	Maltose (% [w/v])
	Low	Medium	High			
25	LV 25	MV 25	HV 25	4	5	0.5
50	LV 50	MV 50	HV 50	4	5	0.5
100	LV 100	MV 100	HV 100	4	5	0.5
250	LV 250	MV 250	HV 250	4	5	0.5
500	LV 500	MV 500	HV 500	4	5	0.5
1,000	LV 1000	MV 1000	HV 1000	4	5	0.5
2,000	LV 2000	MV 2000	HV 2000	4	5	0.5
3,000	LV 3000	MV 3000	HV 3000	4	5	0.5
4,000	LV 4000	MV 4000	HV 4000	4	5	0.5
5,000	LV 5000	MV 5000	HV 5000	4	5	0.5

^a LV = low-viscosity, MV = medium-viscosity, and HV = high-viscosity arabinoxylans (cat. no. P-WAXYL, P-WAXYM, and P-WAXYH, respectively; Megazyme International Ltd., Wicklow, Ireland).

ately after cooling by filling the holding chamber with the test fluids and pressurizing the chamber to $137.9 \text{ kPa} \pm 6.895 \text{ kPa}$ ($20 \text{ psi} \pm 1 \text{ psi}$). Disposable cellulose acetate membrane filters with a pore diameter size of $0.45 \mu\text{m}$ were used.

Cellulose acetate membrane filters (pore diameter size of $0.45 \mu\text{m}$) were used to filter model beers with arabinoxylan concentrations of 100, 500, and 1,000 mg/L and were examined by scanning electron microscopy (SEM) after 5 min of filtration. The filters were plunge-frozen in liquid propane cooled with liquid nitrogen. They were freeze-dried in an Emitech K750 freeze dryer (Emitech, Houston, TX) and held at -60°C overnight at approximately 7.5 Pa ($7.5 \times 10^{-2} \text{ mbar}$). The samples were then gold-coated with an Edwards 306A coater (Edwards, London, U.K.) to a thickness of about 30 nm and examined with a Hitachi S-300N scanning electron microscope (Hitachi, Tokyo, Japan).

Results and Discussion

This study used rheological, filtration, and SEM techniques to examine the physical behavior of arabinoxylan polymers. First, the effect of arabinoxylan concentration, MW, shear rate, and temperature on model beer solution viscosities was determined. Second, the effect of concentration, MW, membrane pore diameter size, and shear history on beer filterability was examined. Finally, cellulose acetate membrane filters were examined by SEM after filtration of arabinoxylan polymer solutions.

The effect of shear rate on the viscosity of model beers was tested with a Bohlin VOR rheometer. Approximate Newtonian behavior was observed with most of the model beers at all

temperatures. Model beers containing the higher concentration of HMW arabinoxylans showed a slight shear-thinning behavior, which is difficult to quantify because of the low sensitivity of the instrument below 100 s^{-1} . At all gum concentrations, LMW arabinoxylans exhibited Newtonian-like behavior.

At low polymer concentrations, the change in apparent viscosity as a function of arabinoxylan concentration was linear, while it became exponential at higher concentrations. The abrupt increase in concentration dependence of apparent viscosity corresponds to the transformation from a dilute to a semidilute solution. The change in the relative viscosity with concentration was examined with the transform of Linemann and Kruger (17) as detailed in Equations 6A and 6B. After applying piecewise regression, with the Systat™ program, to the data, it was found that with low-viscosity arabinoxylans the critical concentration was not reached. The values for medium- and high-viscosity-polymer critical concentrations were found

Table 2. Calculated critical concentration (c^*) and intrinsic viscosity $[\eta]$ values

Arabinoxylans ^a	Molecular weight	c^*		$[\eta]$	
		mg/L	r^2	dL/g	r^2
LVAX	66,000	... ^b	...	1.486 ^c	0.999
MVAX	278,000	1,050.3 ^c	0.990	7.288 ^c	0.998
HVAX	294,000	738.5 ^d	0.996	8.615 ^d	0.996

^a LVAX = low-viscosity arabinoxylans, MVAX = medium-viscosity arabinoxylans, and HVAX = high-viscosity arabinoxylans.

^b c^* not apparent in the concentration range examined.

^c $n = 10$.

^d $n = 9$.

Table 3. Arrhenius dependence of apparent viscosity^a (at approximately 350 s^{-1}) for model beers

Arabinoxylan concentration (mg/L)	LVAX			MVAX			HVAX		
	A^b (mPa·s)	ΔE^c (kJ/mol)	r^{2d}	A^b (mPa·s)	ΔE^c (kJ/mol)	r^{2d}	A^b (mPa·s)	ΔE^c (kJ/mol)	r^{2d}
25	0.237	5.934	0.972	0.171	6.764	0.965	0.179	6.707	0.948
50	0.189	6.536	0.931	0.206	6.337	0.958	0.255	5.855	0.926
100	0.194	6.529	0.910	0.238	6.082	0.935	0.257	5.889	0.889
250	0.188	6.651	0.906	0.225	6.250	0.914	0.260	5.951	0.912
500	0.170	6.997	0.910	0.202	6.622	0.945	0.197	6.793	0.938
1,000	0.228	6.309	0.927	0.197	6.916	0.972	0.162	7.506	0.962
2,000	0.198	6.793	0.952	0.127	8.587	0.954	0.132	8.654	0.931
3,000	0.151	7.576	0.957	0.074	10.437	0.961	0.057	11.320	0.957
4,000	0.138	7.909	0.963	0.036	12.750	0.951	0.023	14.224	0.952
5,000	0.124	8.332	0.961	0.012	16.118	0.956	0.007	18.021	0.951

^a LVAX = low-viscosity arabinoxylans, MVAX = medium-viscosity arabinoxylans, and HVAX = high-viscosity arabinoxylans.

^b A = frequency factor; $n = 4$.

^c ΔE = activation energy; $n = 4$.

^d All correlation coefficient values greater than 0.917 are significant at the $P < 0.05$ levels.

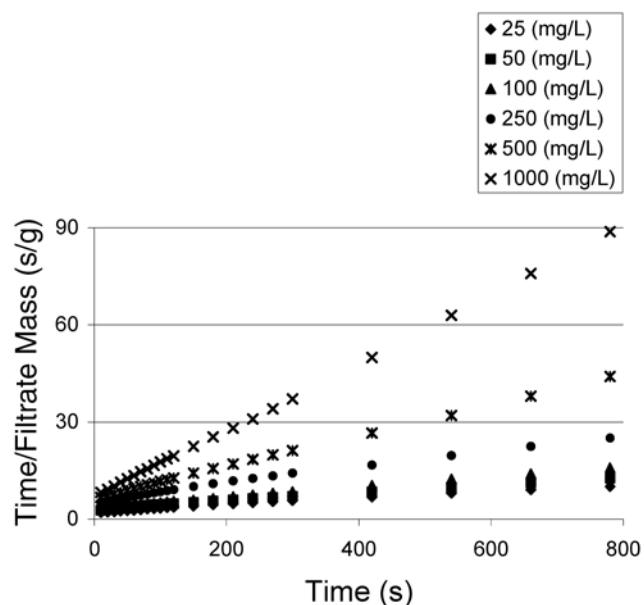


Figure 3. The fit of the Standard blocking law at varying polymer concentrations on medium-viscosity-arabinoxylan model beers ($0.45\text{-}\mu\text{m}$ pore diameter size).

to be 1,050.3 and 738.5 mg/L, respectively (Table 2). The arabinoxylan concentrations used in this study cover a wide range of polymer concentrations reported for worts and beers in earlier studies (22,23). The differences in critical concentration (c^*) among arabinoxylan polymers used in this work most likely reflect the differences in the chain lengths, since they are all reported to have the same arabinose-to-xylose ratio of 41:59 (Megazyme International Ltd.). These results are not surprising and are in accordance with theoretical predictions and previous work of Izydorczyk and Biliaderis (9), who confirmed the increase in critical concentration with the decrease in the MW of arabinoxylan polymers.

Aside from examination of the effect of concentration on the relative viscosity using the $1/\log(\eta_{rel})$ transform, the Kozicki and Kuang (14) method was employed to relate the solution viscosities to gum concentration. This equation (Eq. 3) provides an efficient way for an independent evaluation of the intrinsic viscosity of the studied arabinoxylan polymers. Intrinsic viscosity and b and d parameters were determined by nonlinear regression fitting of the equation to the data with SystatTM 5.05.

It was observed that as the arabinoxylan MW increased, so did its intrinsic viscosity. The difference in the length of the chain backbone or the average MWs of the low-, medium-, and high-viscosity arabinoxylans was confirmed by the limiting viscosity measurements. Since the arabinoxylan polymers had similar arabinose substitution levels, the differences in intrinsic viscosities of these polymers was governed only by the length of the polymer chain. The limiting viscosity numbers $[\eta]$ are presented in Table 2.

The dependence of the intrinsic viscosity on the MWs of arabinoxylan polymers was also determined with the MHKS equation (Eq. 4). The value of the MHKS coefficient was estimated to be 1.14 (standard error of 0.061). This value indicated the re-

stricted flexibility and stiff wormlike conformation of arabinoxylan polymers in model beers. Izydorczyk and Biliaderis (10) reported that the exponent a for rye arabinoxylans was 0.98 and concluded that the polymers had restricted flexibility. In contrast, for barley β -glucan polymers, the exponent a was 0.527 (20), a value characteristic of molecules in a coil-shaped structure.

Apparent viscosities at constant shear rates were examined at 5, 20, 50, and 75°C with a Bohlin controlled stress rheometer. The results showed that the viscosities of model beers at all arabinoxylan concentrations and MW levels tested at approximately 350 s⁻¹ were, in general, independent of shearing time. As expected, the samples were temperature dependent, and the data exhibited an inverse relationship between the viscosity and the absolute temperature. The effect of temperature on viscosity was modeled using an Arrhenius-type relationship:

$$\eta = Ae^{\Delta E/RT} \quad (7)$$

in which η is apparent viscosity, A is the frequency factor, e is the natural logarithm base, ΔE is the activation energy, R is the gas constant, and T is the absolute temperature. The results are summarized in Table 3. As one might expect, the activation energies increased with increasing concentrations and MWs of arabinoxylan polymers, ranging from 5.934 to 18.021 kJ/mol.

To accurately describe the filtration mechanism of small-scale membrane filterability tests, various data transformations were undertaken to allow fit of the various filtration models discussed earlier (7). It was observed that the Sudarmana or Standard blocking law (24) described the data best as evidenced by visual examination of the regression plots and r^2 values. A typical transform of the filtration data to fit the Standard blocking law is shown in Figure 3.

A listing of the V_{max} and Q_{init} values for the various filter and gum concentrations is depicted in Table 4. An analysis of vari-

Table 4. Filtration run results using membranes with various pore diameter sizes

Arabinoxylan concentration (mg/L)	LVAX ^a			MVAX ^a			HVAX ^a		
	V_{max}^b (g)	Q_{init}^c (g/s)	r^2	V_{max}^b (g)	Q_{init}^c (g/s)	r^2	V_{max}^b (g)	Q_{init}^c (g/s)	r^2
0.22- μ m pore diameter size									
25	68.754	0.136	0.99	74.805	0.134	0.99	69.717	0.095	0.99
50	33.021	0.157	0.99	55.167	0.122	0.99	50.012	0.085	0.99
100	11.208	0.091	0.99	39.769	0.119	0.99	31.749	0.066	0.99
250	7.463	0.041	0.99	17.696	0.091	0.99	15.693	0.058	0.99
500	5.355	0.015	0.99	8.682	0.067	0.99	5.571	0.044	0.99
1,000	3.394	0.008	0.99	3.584	0.053	0.99	2.510	0.049	0.99
2,000	2.282	0.003	0.99	1.633	0.028	0.99	0.891	0.017	0.99
0.45- μ m pore diameter size									
25	103.547	0.404	0.99	100.361	0.425	0.99	82.339	0.376	0.99
50	52.877	0.340	0.99	80.984	0.318	0.99	75.758	0.311	0.99
100	23.927	0.320	0.99	62.379	0.299	0.99	57.443	0.245	0.99
250	10.584	0.123	0.98	36.869	0.181	0.99	29.434	0.196	0.99
500	7.033	0.096	0.98	20.770	0.164	0.99	15.221	0.150	0.99
1,000	3.147	0.024	0.97	9.525	0.171	0.99	7.605	0.150	0.99
2,000	2.002	0.006	0.99	3.178	0.130	0.99	2.403	0.078	0.99
0.65- μ m pore diameter size									
25	124.049	0.489	0.98	105.061	0.476	0.97	96.475	0.284	0.97
50	58.140	0.433	0.99	100.505	0.380	0.98	79.611	0.304	0.99
100	28.572	0.552	0.99	70.979	0.346	0.99	62.726	0.287	0.99
250	11.251	0.292	0.99	39.698	0.263	0.99	33.508	0.203	0.99
500	7.116	0.201	0.99	21.187	0.240	0.99	18.060	0.222	0.99
1,000	3.619	0.054	0.98	9.799	0.273	0.99	7.882	0.238	0.99
2,000	1.626	0.013	0.96	4.159	0.174	0.99	3.149	0.159	0.99

^a LVAX = low-viscosity arabinoxylans, MVAX = medium-viscosity arabinoxylans, and HVAX = high-viscosity arabinoxylans.

^b V_{max} = maximum volume of liquid that can be filtered through a membrane filter.

^c Q_{init} = initial flow rate.

ance indicated that the concentration, MW, and filter pore diameter size all had a significant effect on the V_{\max} values ($P < 0.05$). This data may have implications in industrial settings for predicting the filterability of beer in the stages of prefiltration and cold sterile filtration, in which the membranes with pore diameter sizes ranging from 0.2 to 1 μm are used. Interestingly, the medium-viscosity-arabinoxylan model beers had the highest V_{\max} values, while low-viscosity-arabinoxylan model beers had the lowest V_{\max} values at all polymer concentration levels, except at 25 mg/L. It was hypothesized that low-viscosity arabinoxylans, because of their shorter polymer chains, could penetrate the membrane surface more easily than could the larger polymers and, thus, could more quickly clog the membrane pores.

A typical result of the sheared and nonsheared filtration runs are shown in Figure 4, and the complete results are depicted in Table 5. The significant effect ($P < 0.05$) of high-intensity shearing on increasing the filterability of model

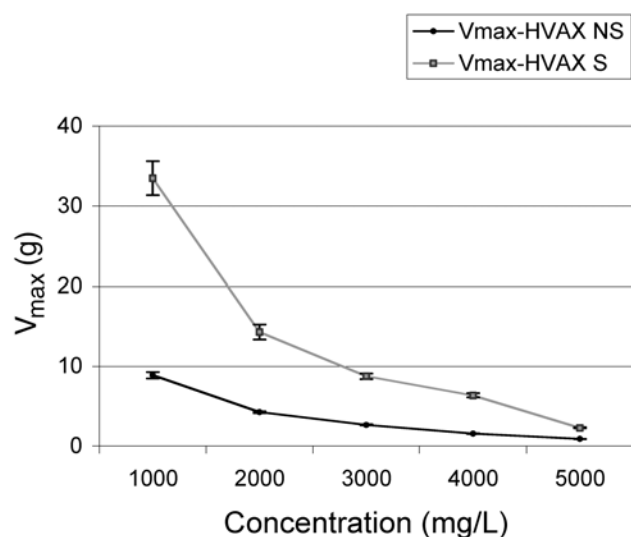


Figure 4. Maximum volume of liquid that can be filtered through a membrane filter (V_{\max}) values for nonsheared (NS) and sheared (S) high-viscosity-arabinoxylan (HVAX) model beers.

beers is most probably the consequence of the destabilization of hydrogen bonds between the unsubstituted portions of the xylan backbone. It is believed that the interchain aggregation between arabinoxylan polymers is stabilized by hydrogen bonds along structurally regular segments of unsubstituted xylan blocks (11). This finding might have some implications in industrial settings since both wort and beer are subjected to shear forces throughout the processing and before the final filtration.

To obtain a better explanation of the filtration mechanism, SEM analysis of filtered membranes was undertaken. Membrane filters with a 0.45- μm pore diameter size for model beers with arabinoxylan concentrations of 100, 500, and 1,000 mg/L were examined after exactly 5 min of filtration.

Caution must be used in drawing conclusions from examination of the electron micrographs. Careful examination of the filter membrane electron micrographs revealed a buildup of a latticelike network of arabinoxylan polymer threads above the filter surface. However, with the increase of polymer MWs in model beers, these networks of threads became more tightly packed. Examination of the electron micrographs suggested that low-viscosity arabinoxylans could penetrate the membrane surface more easily than could medium- and high-viscosity macromolecules because of the shorter polymer chains, thus enhancing the membrane clogging (Fig. 5). This results in a faster reduction of membrane capillary tube diameters because of the adsorption of the precipitates against the walls of these tubes. This seems to be the predominant mechanism of membrane filter plugging, leading to the lowest V_{\max} values of model beers with low-viscosity arabinoxylans. Model beers containing medium- and high-viscosity polymers have a larger portion of macromolecules retained on the membrane surface. It is postulated that the polymers deposited onto the filter surface would eventually blind the membranes, thus preventing fluid from passing through the filter. The filtration results for a polymer concentration of 2,000 mg/L using a membrane with a 0.22- μm pore diameter size support this theory.

While low-viscosity-arabinoxylan model beers had the lowest Q_{init} values, indicating faster pore plugging at the start of the filtration process, medium- and high-viscosity-arabinoxylan model beers had lower V_{\max} values, presumably as a result of a gel building at the membrane surface toward the end of filtration run. However, filtration data for even medium- and high-

Table 5. Filtration run results with model beers

Arabinoxylan concentration (mg/L)	LVAX ^a			MVAX ^a			HVAX ^a		
	V_{\max}^b (g)	Q_{init}^c (g/s)	r^2	V_{\max}^b (g)	Q_{init}^c (g/s)	r^2	V_{\max}^b (g)	Q_{init}^c (g/s)	r^2
Nonsheared model beers									
1,000	7.559	0.140	0.99	13.958	0.879	0.99	8.880	0.530	0.99
2,000	3.820	0.074	0.99	8.211	0.794	0.99	4.243	0.217	0.99
3,000	2.477	0.036	0.98	4.160	0.267	0.99	2.672	0.104	0.99
4,000	1.627	0.019	0.98	2.655	0.126	0.99	1.559	0.040	0.99
5,000	1.041	0.006	0.97	1.722	0.058	0.99	0.888	0.010	0.99
High-intensity sheared model beers									
1,000	11.571	0.433	0.99	48.265	0.997	0.99	33.468	0.676	0.99
2,000	8.961	0.455	0.99	27.106	0.839	0.99	14.277	0.566	0.99
3,000	5.534	0.259	0.99	19.912	0.763	0.99	8.741	0.555	0.99
4,000	2.699	0.058	0.99	11.268	0.696	0.99	6.359	0.463	0.99
5,000	2.193	0.057	0.99	9.565	0.564	0.99	2.290	0.091	0.99

^a LVAX = low-viscosity arabinoxylans, MVAX = medium-viscosity arabinoxylans, and HVAX = high-viscosity arabinoxylans.

^b V_{\max} = maximum volume of liquid that can be filtered through a membrane filter.

^c Q_{init} = initial flow rate.

viscosity-arabinoxylan model beers, using three different membrane pore diameter sizes, were best described with the Standard blocking law. This leads to the conclusion that the membrane pore plugging seems to be the predominant filtration mechanism, even though a portion of arabinoxylan macromolecules are retained at the membrane surface.

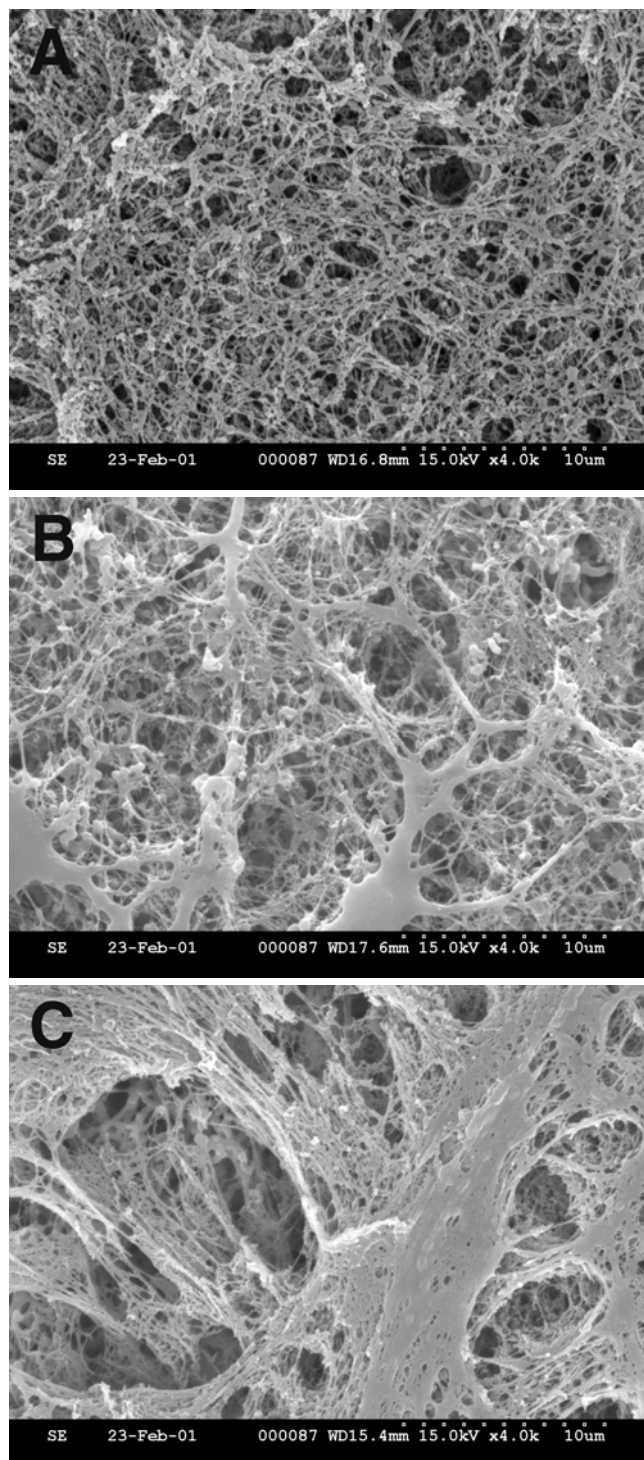


Figure 5. Scanning electron micrograph of membrane surface after filtration with a model beer containing 1,000 mg/L of **A**, low-viscosity; **B**, medium-viscosity; and **C**, high-viscosity arabinoxylans.

The membrane filtration method used in the study for the evaluation of high-intensity shearing on model beer filterability clearly illustrated the effects of arabinoxylan polymer concentration, MW, and high-intensity shearing on V_{\max} (maximum quantity of liquid that can be filtered through a membrane filter) and Q_{init} (initial filtration flow rate). Model beers with arabinoxylan concentrations from 1,000 to 5,000 mg/L were used.

Conclusions

This study investigated the rheological and filtration properties of model beers containing arabinoxylan polymers of three different average MWs (low = 66,000, medium = 278,000, and high = 294,000). A shear rate sweep (36.7 to $1,460$ s^{-1}) at 5 , 20 , 50 , and 75°C indicated approximate Newtonian fluid behavior. It was found that with low-viscosity arabinoxylans the critical concentration was not reached, while the values for medium- and high-viscosity polymers (c^*) were found to be $1,050.3$ and 738.5 mg/L, respectively. The apparent viscosities of the model beers measured at 350 s^{-1} were independent of shearing time. Sample viscosities decreased in an Arrhenius fashion. The activation energies increased with the increasing concentration and MW of arabinoxylan polymers, ranging from 5.934 to 18.021 kJ/mol.

The Sudarmana transformation (24) was used to linearize the filtration data and to calculate the maximum filtrate volume (V_{\max}) and initial rate of filtration (Q_{init}). It was determined that while the arabinoxylan concentration had a significant effect ($P < 0.05$) on reducing V_{\max} and Q_{init} values as the concentration increased, the membrane pore diameter size also had a significant effect ($P < 0.05$) on increasing V_{\max} and Q_{init} values as the pore diameter size increased. It was interesting to note that while arabinoxylan MW had a significant ($P < 0.05$) effect on V_{\max} and Q_{init} values, medium-viscosity-arabinoxylan model beers had the highest V_{\max} values, while low-viscosity-arabinoxylan model beers had the lowest V_{\max} values on all polymer concentration levels, except at 25 mg/L.

SEM of the results indicated that low-viscosity arabinoxylans could penetrate the membrane surface more easily than could medium- and high-viscosity macromolecules because of the shorter polymer chains, thus enhancing the membrane clogging. The evaluation of high-intensity shearing (at $>5,000$ s^{-1}) on model beer filterability clearly illustrated the significant effects ($P < 0.05$), with high-intensity shearing increasing V_{\max} and Q_{init} values.

The findings from this study increase the malting and brewing industries knowledge of arabinoxylan polymer behavior during processing. Although these polymers, in the concentration range normally found in wort and beer, largely behave like Newtonian fluids, they have a great potential for causing production problems at different stages of wort and beer filtration. Filtration studies also elucidate the mode of membrane plugging of arabinoxylan macromolecules with different MWs.

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